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ESTIMATION OF KINETIC PROPERTIES OF PARTICLES FORMING RANDOM ROUGH SURFACES

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An investigation of kinetic properties (diffusion length and activation energy) for deposited particles that form films with rough surfaces is presented. Calculation of these properties is performed as a function of the roughness exponent H, the rms-roughness σ and the in-plane correlation length ξ of the final film surface morphology. The diffusion length scales as $d \propto \xi/\sigma^{1/H}$ for $0 < H \leq 1$ and possess an exponential behaviour $d \propto e^{1/\sigma^2}$ for $H = 0$ with a low sensitivity on ξ. We illustrate our calculations for room temperature evaporated Ag films, where the estimated diffusion lengths are $d \sim 2$–3 nm and the corresponding activation energies $E < 1$ eV. © 1997 Elsevier Science Ltd.

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During the growth of thin films the final surface morphology is determined by the competition between surface relaxation mechanisms and atom arrival rate. Fundamentally the process is a nonequilibrium one where the initial non-occupied surface evolves in time to attain a new state with the surface covered by the incident atoms. An understanding of the mass transport across the surface by means of surface diffusion is of crucial importance for controlling atomic processes on well-prepared surfaces.

A wide variety of thin films grown under non-equilibrium conditions (e.g. vapour deposited thin metal films) possess surfaces with roughness which is described in terms of self-affine fractal scaling [1, 2]. This type of roughness is characterized by the roughness exponent H ($0 < H < 1$), the rms roughness σ and the in-plane correlation length ξ. The ratio σ/ξ describes mainly the long-wavelength ($> \xi$) roughness characteristics. Finer roughness details at short-wavelengths ($< \xi$) are revealed through the effect of the exponent H (or a local fractal dimension $D = 3 - H$) [2–4] which describes the degree of height–height fluctuation density such that small values of H ($H \sim 0$) correspond to highly irregular surfaces, while large values ($H \sim 1$) correspond to surfaces with a smooth hill-valley structure (see Fig. 1) [1].

In our study, kinetic characteristics such as diffusion length and activation energy of deposited metal adatoms, that form thin films with rough surfaces, will be related directly to the nanoscale roughness characteristics (σ, ξ, H) of the final film morphology. Indeed, a detailed investigation of the relation between roughness parameters of the final film morphology and diffusion-kinetic characteristics that lead to this morphology is still in its infancy. Moreover, we illustrate our calculations by estimating diffusion lengths and activation energies for Ag thin films studied by means of scanning tunnelling microscopy (STM) and comparisons are performed to previous diffusion studies.

In recent diffusion studies of Ag films, the transient mobility diffusion length d_0 (which is independent of growth conditions) was introduced to explain low measured activation energies [5, 6]. This mobility was explained in terms of the curvature of the substrate interatomic potential. Indeed, for a stiff substrate (strong atom bonds), the excess of energy an atom has in the gas phase (before it condenses onto the surface) can be transferred into lateral motion since it is not absorbed immediately. Thus, the particle is allowed to perform extra jumps which is the source of d_0. It was suggested that d_0 can be

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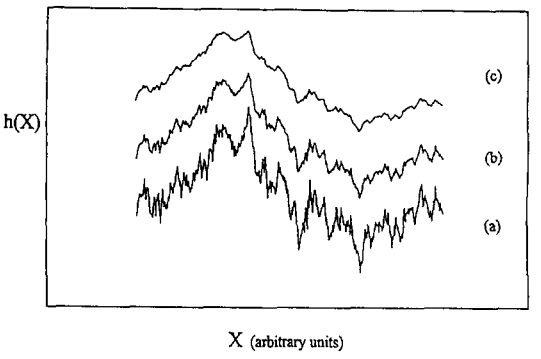

Fig. 1. Schematics of the surface height profile $h(X)$ vs X for various values of the roughness exponent H: (a) $H = 0.3$, (b) $H = 0.5$, (c) $H = 0.7$. The corresponding local fractal dimension is $D = 3 - H$ for two-dimensional substrates and $D = 2 - H$ for one-dimensional substrates.

of the order of ~5 nm [5], which is similar in magnitude with preliminary estimations of the diffusion length (~2 nm) from roughness characteristics of Ag films [7].

The diffusion length (d) is defined as the distance a particle travels upon arrival on the surface before it is incorporated into the already existing aggregate. Thus, if the particle travels a distance d, it is plausible to consider a change of the surface width $\sigma(d)$ (rms-roughness over an area d^2) approximately by half the atomic step a_0 [7] or $\sigma(d) \approx a_0/2$. The fluctuation in the surface height only due to fluctuations in the beam intensity (random noise) can be estimated as follows. For film of thickness h/a_0 over an area $(d/a_0)^2$, the average number of deposited atoms is $N \approx [(d/a_0)^2(h/a_0)]$ and the height fluctuation (in the absence of any relaxation mechanism of the incoming particles) $N^{1/2}/(d/a_0)^2 = (h/a_0)^{1/2}/(d/a_0)$ [8]. Thus, if for a particular film morphology $\sigma(d)/a_0 < (h/a_0)^{1/2}/(d/a_0)$ the presence of a surface relaxation mechanism can be conjectured.

In terms of the scaling theory approach [2] developed to describe growth under nonequilibrium conditions, the rms-roughness during growth over a substrate of planar size L and film thickness h scales as $\sigma(L, h) = L^H F(h/L^z)$ with $F(x) \sim x^b$ if $x \ll 1$ and $F(x) \sim$ const if $x \gg 1$. z and b are respectively the dynamic and growth scaling exponents such that $z = H/b$ (b, $z > 0$). Since $\sigma(L) = \sigma(L, \infty) = L^H F(\infty)$ and $\sigma(L \geq \xi) \approx \sigma$, we obtain $F(\infty) \approx \sigma/\xi^H$ which in combination with $\sigma(d) \approx a_0/2$ yields $d \approx \xi/(\sigma/a_0)^{1/H}$ where the ratio $\xi/\sigma^{1/H}$ represents a measure of the atomic step density [9]. Although scaling theory yields the correct behaviour of the diffusion length for $H > 0$, it fails for small values of $H (H \sim 0)$ since a more precise calculation of the surface width is needed due to the increased importance of discreteness effects with decreasing H and especially in the limit $H = 0$ where logarithmic behaviour appears.

The film surface is defined by a vertical height profile over the horizontal xy-plane and is represented by a single valued function $h(R)$ of the in-plane position vector $R = (x, y)$. For a self-affine fractal surface the surface width $\sigma(L) = \langle [h(R) - \langle h(R) \rangle]^2 \rangle^{1/2}$ (over an area $L \times L$) scales as $\sigma(L) \sim L^H$ if $L \ll \xi$ and $\sigma(L) \approx \sigma$ if $L \gg \xi$ [2]. This behaviour is satisfied by the analytic expression of $\sigma(L)$ (in terms of the *k-correlation* model) [10]

$$\sigma(L) = [\sigma/(2Ha)^{1/2}][(1 + ak_L^2\xi^2)^{-H} - (1 + ak_c^2\xi^2)^{-H}]^{1/2}, \quad (0 < H \leq 1), \tag{1}$$

$$\sigma(L) = [\sigma/2a)^{1/2}][\ln\{(1 + ak_c^2\xi^2)/(1 + ak_L^2\xi^2)\}]^{1/2}, \quad (H = 0), \tag{2}$$

where $k_c = \pi/a_0$ and $k_L = 2\pi/L$. The parameter "a" in equations (1) and (2) is given by $a = (1/2H)[1 - (1 + ak_c^2\xi^2)^{-H}]$ if $0 < H < 1$ and $a = (1/2)\ln(1 + ak_c^2\xi^2)$ if $H = 0$.

Upon substitution of $\sigma(L)$ from equations (1) and (2) into $\sigma(d) \approx a_0/2$, we obtain the diffusion length (d) as a function of the roughness parameters σ, ξ and H

$$d \approx 2\pi\xi a^{1/2}[F(H)^{1/H} - 1]^{-1/2};$$

$$F(H) = (aHa_0^2/2\sigma^2) + (1 + ak_c^2\xi^2)^{-H}, \quad (0 < H \leq 1), \tag{3}$$

$$d \approx 2\pi\xi a^{1/2}[F(0) - 1]^{-1/2};$$

$$F(0) = e^{-aa_0^2/2\sigma^2}(1 + ak_c^2\xi^2), \quad (H = 0). \tag{4}$$

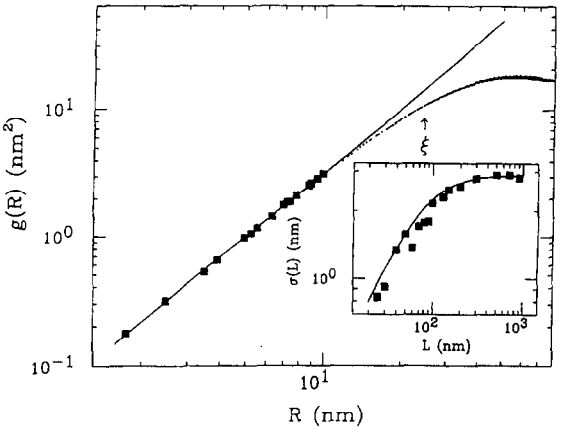

Fig. 2. Correlation data $g(R)$ ($\sim R^{2H}$; $R \ll \xi$) for the Ag film where power law fit gives $H = 0.84 \pm 0.006$. The vector shows the position of the correlation length ξ. The inset presents, surface width data (squares) of the same Ag film where the solid-line depicts a calculation of $\sigma(L)$ vs L in terms of eqn (1) with $H = 0.84$, $\xi = 22$ nm (which corresponds to the *k-correlation model* [10]) and $\sigma = 2.88$ nm obtained from the saturation regime of $g(R)$.

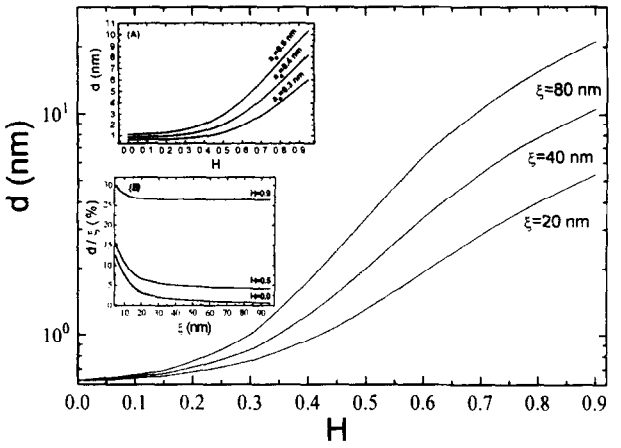

Fig. 3. Calculations of d vs the roughness exponent H from equations (3) and (4) for $a_0 = 0.3$ nm, $\sigma = 2$ nm, $\xi = 20$, 40, 80 nm and values of H in the range $0 \leq H < 1$. The inset (A) shows d vs H for various values of the atomic step $a_0 = (0.3, 0.4, 0.5)$ nm, $\xi = 20$ nm, and $\sigma = 2$ nm. The inset (B) shows $d\xi$ (%) vs ξ for various roughness exponents H, $a_0 = 0.3$ nm and $\sigma = 2$ nm.

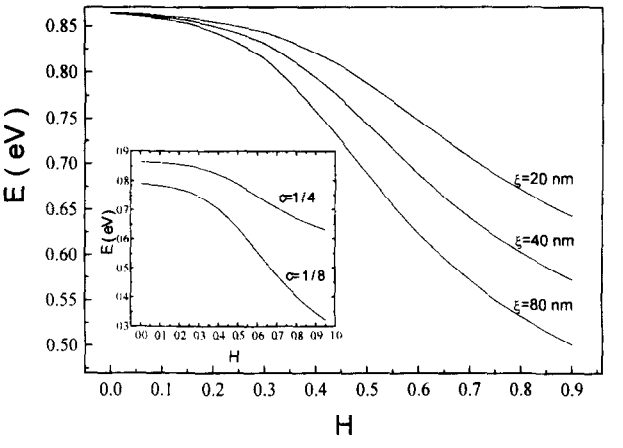

Fig. 4. Calculations of E vs H for $T = 300$ K, $A_0 = 7.89 \times 10^{13}$ Hz, $c = 1/4$, $a_0 = 0.3$ nm, $\sigma = 2$ nm, $\xi = 20$, 40, 80 nm. The inset shows the effect of the exponent "c" on E as a function of H for $T = 300$ K, $A_0 = 7.89 \times 10^{13}$ Hz, $a_0 = 0.3$ nm, $\xi = 20$ nm and $c = 1/4$, $1/8$.

For $a_0 \ll d \ll \xi$ and $H > 0$, $a \approx 1/2H$ and equation (3) yields $d \approx (2\pi^2/H)^{1/2}\xi(a_0/2\sigma)^{1/H}$. This is the same scaling behaviour $d \approx \xi/(\sigma/a_0)^{1/H}$ predicted previously from the scaling theory apart from a prefactor that depends on the particular surface model for $\sigma(L)$.

Figure 2 shows height-difference correlation function data acquired by means of Scanning Tunnelling Microscopy (STM) for a room temperature Ag film of thickness $h = 208$ nm, which allow precise determination of the parameters H, σ and ξ. The exponent $H = 0.84 \pm 0.006$ is obtained from the linear fit (in the regime of length scales $0 < R < 0.4\xi$) of the height-difference correlation function $g(R)$ with $\xi \approx 22$ nm that corresponds to the value $g(R = \xi)$ (in terms of the *k-correlation* model) [7, 10]. The value of the correlation length is of physical significance since it compares to cluster sizes observed in the STM images. The inset shows surface width data $\sigma(L)$ vs L for the same film and a calculation of $\sigma(L)$ vs L in terms of equation (1) with $H = 0.84$, $\xi = 22$ nm and $\sigma = 2.88$ nm.

For the Ag film of Fig. 2 ($\xi = 22$ nm, $\sigma = 2.88$ nm, $H = 0.84$, $a_0 = 0.27$ nm), equation (3) yields the diffusion length $d \approx 3$ nm which is approximately ten atomic steps ($\sim 10a_0$) and $\sim 15\%$ of the in-plane correlation length ξ. Moreover, this value of the diffusion length (~ 3 nm) compares with values assigned to the transient mobility diffusion length d_0 (~ 5 nm) [5]. Similar values of the diffusion length ($d \approx 2$ nm) were obtained for a wide range of room temperature grown Ag films in the thickness range 10–700 nm [7]. Indeed, the ratio $\xi/\sigma^{1/H}$ (and thus the diffusion length d) remains constant if $\sigma = A_1 h^b$ and $\xi = A_2 h^{1/z}$ with $z = H/b$ ($H = \text{const}$) as is predicted by the scaling theory [2] and confirmed in previous studies of Ag films [7].

Figure 3 depicts calculations of the diffusion length d as a function of H for $0.025 \leq \sigma/\xi \leq 0.1$. As the roughness exponent H increases, the diffusion length acquires significant values ($d \gg a_0$) for $H > 0.5$. Large values of the diffusion length ($\gg a_0$) for large roughness exponents $H(\geq 0.6)$ are in agreement with growth model predictions which incorporate surface diffusion as the dominant relaxation mechanism and yield $0.6 < H < 1$ [11]. The rapid growth of the diffusion length for exponents $H > 0.6$ is strongly enhanced for small ratios σ/ξ ($\ll 1$) which give rise to smoother surfaces at long wavelengths. The insensitivity of d with respect to σ/ξ for small H (~ 0) can be seen directly from equation (4) which yields $d \approx (2\pi/k_c)\exp(a_0^2 a/2\sigma^2)$ ($d \ll \xi$). The sensitivity of d on the atomic step a_0 can be seen in Fig. 3 [inset (A)]. Although the diffusion length estimated in this manner is less than 30% of the roughness correlation length ξ [Fig. 3, inset (B)], it still remains a significant fraction of the latter.

Furthermore, from the diffusion length d we can estimate the associated activation energy. For random deposition of atoms at a rate Ja_0^2 per substrate site (J is the atom flux), the atom migration is considered as a nearest-neighbour hopping process with a rate given by an Arrhenius law $A(E, T) = A_0 \exp(-E/k_B T)$ [12, 13]. A_0 is an attempt rate, E the energy barrier for hopping and T the substrate temperature. Typical values for deposition rate J are in the range 1–0.01 ML s^{-1} (ML: monolayers). The prefactor A_0 is taken to be $A_0 \approx 4\pi k_B T/\hbar$ [12] so that it is of the order of the typical vibrational frequency which for $T = 300$ K yields $A_0 \approx 8 \times 10^{13}$ Hz. Since

$d/a_0 \approx (D/Ja_0^2)^c$ with $D \approx a_0^2 A(E,T)$ the diffusion constant [13, 14], we obtain $E \approx k_B T[\ln(A_0/J) - c^{-1}\ln(d/a_0)]$. The value of the exponent "c" in general varies with coverage and growth conditions. A linear BCF (Burton–Cabrera–Frank) theory would yield $c = 1/4$ [13]. However, the nonlinearities that are involved under true growth conditions would lead to a departure from this value. Indeed, values in the range $1/8 < c < 1/4$ were predicted for low coverages (<1 ML) [13].

Figure 4 shows the activation energy E vs H for ratios σ/ξ in the range $0.025 \leq \sigma/\xi \leq 0.1$. As the value of the exponent c decreases, the activation energy decreases (see inset of Fig. 4) especially in the regime of large H ($H > 0.5$) where the diffusion length grows rapidly with H (Fig. 3). For the Ag film of Fig. 2 where $J = 0.012$ ML s^{-1} we have $d \approx 3$ nm and the activation energy is estimated to be $E \sim (0.4$–$0.7)$ eV (for $c = 1/4$ and 1/8 respectively). Activation energies in the range (0.1–1) eV have been obtained in recent diffusion studies for very thin Ag films on various substrates, substrate-temperatures and coverages; e.g. Ag/Si(1 1 1) ($E \sim 0.25 \pm 0.03$ eV) [5], Ag/Ge(1 1 1) ($E \sim 0.78$–0.87 ± 0.04 eV) [15], Ag/Ag(1 1 1) ($E \sim 0.1$ eV) [16].

In conclusion, the diffusion length d for particles forming rough self-affine fractal surfaces was estimated as a function of the characteristic roughness parameters H, σ and ξ. The estimated diffusion lengths can be a significant fraction of the roughness correlation length as is revealed with direct comparison for Ag films. Our comparison with previous surface diffusion studies revealed that the calculated diffusion length is close to that associated with the transient mobility length d_0, however, further experimental (on different substrates and growth temperatures) and theoretical studies will be required to resolve this issue. Finally, the associated activation energy was estimated and leads for Ag films to values (despite the arbitrariness of the exponent "c") that are similar in order with those observed in former diffusion studies of Ag systems.

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